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RESEARCH FOUNDATION

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM

by

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FOREWORD

This work was carried out at The Ohio State University Cryogenic Laboratory under Contract with U.S. Navy, Office of Naval Research Contract Number N6onr-225, Task Order IV, ONR Project Number NR 058 038, with The Ohio State University Research Foundation. This report covers information obtained during the study entitled: " Low Temperature Thermodynamics of Inorganic Substances". It represents the 22nd Technical Report of this series.

Director - H.L. Johnston

Editor - Esther R. Fultz

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then transferred to a vacuum desiccator in which the desiccant was crude ammonium chromium alum partially dehydrated by heating at 100° C for several hours. The wet and dry forms of the alum were allowed to equilibrate for several months while other work was in progress. Analyses were made at intervals by complete dehydration of weighed samples in an oven set at 400° C, in order to test the approach to equilibrium. (This alum normally loses nine of its twelve moles of water of crystallization at 100° C and the other three moles at 300° C.) The final sample contained 45.01 % H_2O (theoretical = 45.19 %); 48.7269 grams (0.10186 mole) of this material were sealed in Calorimeter No. 6, one of a group of seven calorimeters[3] of identical design in use in This Laboratory.

Sample II was prepared in 1952 under exactly the same conditions as those of the previous sample. Analyses showed that it contained 45.45 % H_2O (theoretical = 45.19 %) and weighed 51.466 grams (0.1076 mole). It was sealed in Calorimeter No. 3 of the same group of calorimeters mentioned above. Data for the heat capacities obtained from the 1949 and 1952 measurements are shown graphically in Figure 1.

PROCEDURE AND EXPERIMENTAL RESULTS

The experimental results obtained in 1949 are summarized in Table I. No transition was found in the heat capacity measurements, but the experimental point at 93.87° K (taken with a ΔT of 8.362) was anomalously high when observed on a smooth plot of these data.

In 1952, the original sample (Sample I) prepared in 1949 was cooled down to 75° K and allowed to remain at this temperature for two days. The heat capacity measurements were then carried out from 75° to 101° K, with smaller temperature intervals, as shown in Table II. A region of anomalously high heat capacities was found between 92° and 98° K. The sample was again cooled down to 81° K and after it had remained at 81° K for about two days, a second series of heat capacity measurements was started. In the second series, the peak of this anomalously high region of the heat capacity curve showed a slight shift towards the high temperature end, relative to that of the first series; presumably, this was due to hysteresis. To eliminate the possibility that some slow change might have taken place in the sample between 1949 to 1952, a new sample (Sample II) containing slightly more water

FIG. 1 - HEAT CAPACITY OF AMMO ■ NIUM CHROMIUM ALUM

TABLE I

HEAT CAPACITY ... AMMONIUM ... CHROMIUM ALUM

$(NH_4)\,Cr\,(SO_4)_2 \cdot 12H_2O$

Mole Wt = 478.36 (1949 ... 0.10186 Moles

Mean T		C_p cal/mole/deg
17.26		
16.75		
19.91		
21.00		
22.69		
25.08		
27.[illegible]		
29.93		
32.37		
35.43		
39.07		
42.92		
47.14		
51.76		
56.25		
63.78		
70.07		
77.64		
85.51		
87.33		
93.87		
101.28		
109.20		
119.53		
129.51		
137.99		
145.66		
152.91		
161.62		
172.32		
182.52		

TABLE I
(continued)

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM
$(NH_4)\ Cr\ (SO_4)_2 \cdot 12H_2O$

Mole Wt = 478.36 0.10186 Moles

(1949 data)

Mean T °K	ΔT	C_p cal/mole/deg
192.85	10.894	115.98
199.02	5.853	118.99
204.42	12.042	121.96
206.83	8.978	123.41
214.30	7.326	126.70
217.14	13.073	128.36
220.51	8.288	129.90
222.51	8.804	130.91
228.36	3.770	133.66
229.92	11.924	135.07
234.80	7.887	137.01
242.65	13.096	139.35
254.36	10.353	145.38
264.45	9.722	150.37
274.07	9.134	156.06
282.72	7.120	160.36
292.24	7.597	165.18
304.44	7.973	170.22

TABLE II

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM
$(NH_4)Cr\ (SO_4)_2 \cdot 12H_2O$

(1952 data)

Mean T °K	ΔT °K	C_p cal/mole/deg	Mean T °K	ΔT °K	C_p cal/mole/deg
Sample I, cooled for 2 days before starting measurements (50.454 gm, 0.1055 moles)					
76.59	2.299	48.77	91.78	2.838	60.83
78.60	1.833	49.95	92.88	1.577	61.38
80.53	1.750	51.59	93.77	1.178	203.99
82.25	1.686	52.68	94.43	1.297	178.50

TABLE II
(continued)

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM
$(NH_4)Cr(SO_4)_2 \cdot 12H_2O$
(1952 data)

Mean T °K	ΔT °K	C_p cal/mole/deg	Mean T °K	ΔT °K	C_p cal/mole/deg
Sample I, cooled for 2 days before starting measurements (50.454 gm, 0.1055 moles)					
83.90	1.632	53.68	95.28	2.271	82.78
85.35	1.595	54.51	95.33	2.030	96.74
86.94	1.543	55.49	96.01	1.795	115.13
88.46	1.499	56.35	97.64	2.519	65.64
89.94	1.457	57.35	100.13	2.451	65.34
91.39	1.413	58.36			
Sample II, cooled for two days before start ng measurements (51.466 gm, 0.1076 moles)					
81.72	1.819	52.46	93.73	2.014	132.95
84.12	2.987	53.42	95.99	2.133	119.69
87.50	3.773	55.56	98.64	3.114	63.48
91.14	3.529	58.36			
Sample II, measurements started immediately after the sample had cooled to about 90°K.					
91.07	2.756	58.28	97.15	12.773	62.33
94.60	4.301	60.46	98.74	4.004	63.00

TABLE II
(continued)

HEAT CAPACITY OF AMMONIUM CHROMIUM ALUM
$(NH_4)Cr(SO_4)_2 \cdot 12H_2O$
(1952 data)

Mean T °K	ΔT °K	C_p cal/mole/deg	Mean T °K	ΔT °K	C_p cal/mole/deg
Sample I, cooled for 2 days before starting measurements (50.454 gm, 0.1055 moles)					
83.90	1.632	53.68	95.28	2.271	82.78
85.35	1.595	54.51	95.33	2.030	96.74
86.94	1.543	55.49	96.01	1.795	115.13
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89.94	1.457	57.35	100.13	2.451	65.34
91.39	1.413	58.36			
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91.07	2.756	58.28	97.15	12.773	62.33
94.60	4.301	60.46	98.74	4.004	63.00

was prepared and a fourth series of heat capacity measurements was carried out under conditions identical to those for the second and third series. The same transition, spread over the same temperature region (92° to 97°K), was found in this fourth series of measurements. In order to correlate the results observed in 1949, a fifth series of heat capacity measurements (on Sample II) was started immediately after it had reached 90°K. The transition disappeared under these conditions. It is therefore concluded that the near disappearance of the transition in the 1949 observations was due to super-cooling of the sample. Since in the 1949 measurements, data below 80°K were taken in a series of runs subsequent to those above liquid air temperatures, and after the sample had been cooled for more than a day at 65°K, we believe that the values obtained from 14° to 65°K in our 1949 measurements do give the true heat capacities of this low temperature form of the crystal. This conclusion is further justified from our heat of transition measurements in which it is observed (Table III) that data taken after the sample remained at 85°K for eight hours are identical within error limits, to those taken with longer equilibrium periods.

The heat of transition was obtained in the usual way, i.e., by subtracting from the total amount of energy input that part of energy which was used for heating the sample. Four determinations were made with the sample kept at 85°K for different lengths of time, prior to the runs.

The thermodynamic functions derived from the smooth heat capacity curve (using Table II data in the interval 80 to 100°K), are given in Table IV at integral values of temperature. The entropy at 298.16°K is 171.93 ± 1.00 e.u. of which 0.64 e.u. was obtained by extrapolating below 18°K using a C_p versus log T plot.

DISCUSSION OF RESULTS

Kraus and Nutting have studied the spectra of a large number of chrome alums at low temperatures. They found that it was often possible to keep an ammonium sulfate alum crystal in its original perfect, highly transparent condition when placed in liquid nitrogen or liquid hydrogen. In this case the spectra at the higher and lower temperatures differ only in the line breadth. On other occasions, an apparently perfect crystal retains its transparency for a few minutes

TABLE III

THE HEAT OF TRANSITION OF AMMONIUM CHROMIUM ALUM
$(NH_4)\ Cr\ (SO_4)_2\ \ 12H_2O$

Run No.	t^a hr	Heat of Transition cal/mole
1	8	267.58
2	16	267.61
3	46	279.90
4	100	267.10
	Average	267.43 ± 0.13^b

(a) t is the time for which the sample had been cooled before starting measurements of the heat of transition.

(b) Run No. 3 has not been used for calculating the average value of heat of transition.

TABLE IV

THERMODYNAMIC FUNCTIONS OF AMMONIUM CHROMIUM ALUM
$(NH_4)\ Cr\ (SO_4)_2\ \ 12H_2O$

T °K	C_p cal/mole/deg	$S-S_o$ cal/mole/deg	$-(H-H_o)/T$ cal/mole/deg	$-(F-H_o)/T$ cal/mole/deg
Solid I				
25	9.10	5.13#	3.183#	1.95
50	29.35	17.73	11.219	6.51
75	48.19	33.20	20.42	12.78
Transition occurs between 92° - 97° K				
Solid II				
100	64.53	52.00	31.98	20.02
125	79.14	67.96	39.95	28.01
150	93.02	83.62	47.64	35.98
175	106.73	99.00	55.12	43.88
200	119.74	114.11	62.39	51.72
225	132.99	128.93	69.45	59.48
250	144.15	143.47	76.32	67.15
275	156.36	157.78	83.04	74.74
298.16	168.55	170.89	89.19	81.70
300	169.26	171.93	89.68	82.25

$(H-H_o)$ extrapolated to 0°K

after being placed in the cooling liquid and then almost instantaneously becomes practically opaque, as though broken into an infinite number of tiny crystals by the disruption of the lattice. It is these nearly opaque crystals, which Kraus and Nutting called "shattered" crystals that give absorption spectra at high temperatures which are quite different from those at low temperatures.

We give the following explanation for our heat capacity data in terms of Kraus and Nutting's observations: The 1949 data, which show no transition, correspond to the crystals (supercooled) which preserve their original transparent high temperature form, while the 1952 data, on the other hand, correspond to what Kraus and Nutting call "shattered crystals." We presume that the transition is accompained by a volume change which, under condition of hysteresis, produces a multicrystalline material.

ACKNOWLEDGEMENT

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